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Synthesis, characterization and crystal structures of the bidentate Schiff base *N*,*N*′-bis(2-nitrocinnamaldehyde)ethylenediamine and its complex with CuNCS and triphenylphosphane

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Reaction of copper(I) thiocyanate and triphenylphosphane with the bidentate Schiff base *N*,*N*′-bis(*trans*-2-nitrocinnamaldehyde)ethylenediamine {Nca_2en, (1); systematic name (1*E*,1′*E*,2*E*,2′*E*)-*N*,*N*′-(ethane-1,2-diyl)bis[3-(2-nitrophenyl)prop-2-en-1-imine]}, $C_{20}H_{18}N_4O_4$, in a 1:1:1 molar ratio in acetonitrile resulted in the formation of the complex {(1*E*,1′*E*,2*E*,2′*E*)-*N*,*N*′-(ethane-1,2-diyl)bis[3-(2-nitrophenyl)prop-2-en-1-imine]-κ^2N,*N*′}(thiocyanato-κN)(triphenylphosphane-κP)copper(I)], [Cu(NCS)($C_{20}H_{18}N_4O_4$)($C_{18}H_{15}P$)] or [Cu(NCS)(Nca_2en)(PPh_3)], (2). The Schiff base and copper(I) complex have been characterized by elemental analyses, IR, electronic and ^{1}H NMR spectroscopy, and X-ray crystallography [from synchrotron data for (1)]. The molecule of (1) lies on a crystallographic inversion centre, with a *trans* conformation for the ethylenediamine unit, and displays significant twists from coplanarity of its nitro group, aromatic ring, conjugated chain and especially ethylenediamine segments. It acts as a bidentate ligand coordinating *via* the imine N atoms to the Cu^I atom in complex (2), in which the ethylenediamine unit necessarily adopts a somewhat flattened *gauche* conformation, resulting in a rather bowed shape overall for the ligand. The NCS^- ligand is coordinated through its N atom. The geometry around the Cu^I atom is distorted tetrahedral, with a small N—Cu—N bite angle of 81.56 (12)° and an enlarged opposite angle of 117.29 (9)° for SCN—Cu—P. Comparisons are made with the analogous Schiff base having no nitro substituents and with metal complexes of both ligands.

1. Introduction

Metal complexes containing Schiff base ligands have been of great interest for many years; the Cambridge Structural Database (Version 5.35, December 2013, plus updates to May 2014; Allen, 2002; Groom & Allen, 2014) contains over 160 entries having the Schiff base skeleton *R*—CH═N—CH_2CH_2—N═CH—*R*, in which *R* is any alkyl or aryl group, and has nearly 1800 metal complexes of such ligands. These compounds play an important role in the development of coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures (Bhatia *et al.*, 1981; Costamagna *et al.*, 1992). The coordination chemistry of copper(I) complexes is of interest due to their potential application in catalytic processes, photosensitization reactions, light-harvesting studies and the design of supramolecular arrays (Zubieta *et al.*, 1983; Kirchner *et al.*, 1987). The steric, electronic and conformational effects imparted by the coor-

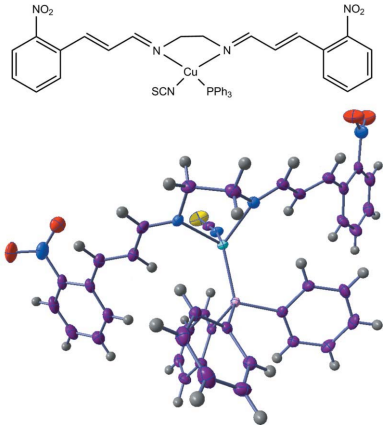
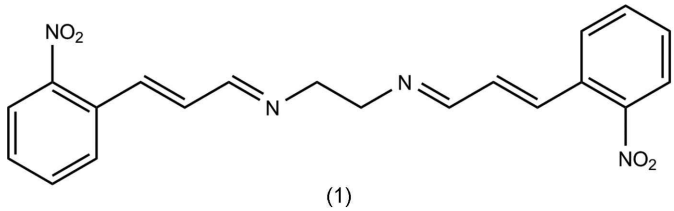


Table 1
Experimental details.

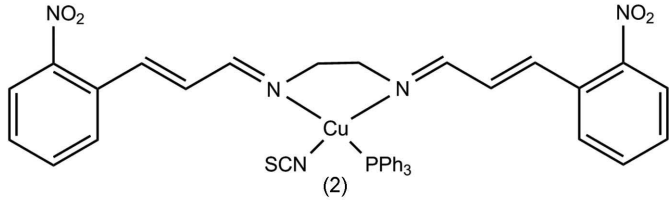
	(1)	(2)
Crystal data		
Chemical formula	$C_{20}H_{18}N_4O_4$	$[Cu(NCS)(C_{20}H_{18}N_4O_4)(C_{18}H_{15}P)]$
M_r	378.38	762.27
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, $P\overline{1}$
Temperature (K)	120	150
a, b, c (Å)	11.441 (7), 3.781 (2), 20.553 (12)	9.1038 (8), 13.8186 (12), 15.2972 (14)
α, β, γ (°)	90, 97.444 (10), 90	104.7831 (14), 102.6778 (14), 91.3000 (14)
V (Å^3)	881.6 (9)	1809.0 (3)
Z	2	2
Radiation type	Synchrotron, λ = 0.6727 Å	Mo $K\alpha$
μ (mm^{-1})	0.10	0.75
Crystal size (mm)	0.10 × 0.08 × 0.01	0.34 × 0.30 × 0.30
Data collection		
Diffractometer	Bruker APEXII CCD diffractometer	Bruker SMART 1K CCD diffractometer
Absorption correction	Multi-scan (*TWINABS*; Sheldrick, 2008*a*)	Multi-scan (*SADABS*; Sheldrick, 2008*a*)
T_{min}, T_{max}	0.90, 1.00	0.75, 0.81
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8304, 3085, 2804	14710, 7308, 6786
R_{int}	0.042	0.025
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.626	0.625
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.125, 0.97	0.069, 0.130, 1.35
No. of reflections	3085	7308
No. of parameters	128	460
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.19, −0.19	0.76, −0.65

Computer programs: *APEX2* (Bruker, 2006), *SMART* (Bruker, 2006), *SAINT* (Bruker, 2006), *SHELXTL* (Sheldrick, 2008*b*), *DIAMOND* (Brandenburg, 2012) and *SHELXL2014* (Sheldrick, 2015).

dinated ligands play an important role in modifying the properties of metal complexes (Meghdadi *et al.*, 2002; Jin *et al.*, 1999). Linkage isomerism is a phenomenon that is characteristic of transition metal complexes, whereby ambidentate ligands are capable of coordination through different binding sites. A large variety of linkage isomers involving ligands such as NCO^-, NCS^-, $NCSe^-$, CN^-, NO^-, NO_2^- and SO_3^-, mostly in mononuclear complexes, have been reported in recent years (Golchoubian *et al.*, 2013; Machura *et al.*, 2012). In this paper, we report the synthesis, spectroscopic characterization and crystallographic structural study of the Schiff base *N*,*N*′-bis(*trans*-2-nitrocinnamaldehyde)ethylenediamine (Nca_2en), (1), and its Cu^I complex, (2), containing also triphenylphosphane and isothiocyanate as ligands (see Scheme 1), and compare this complex with others containing the same ligand and its analogue without nitro groups. Although the structures of 11 complexes of (1) as a ligand with cobalt, nickel, copper, zinc and silver have been reported (Kirchner *et al.*, 1987; Dehghanpour, Mahmoudi, Sepaveh & Ng, 2006; Dehghanpour & Mahmoudi, 2007; Habibi, Montazerozohori *et al.*, 2007; Dehghanpour, Mahmoudi & Haghighatseresht, 2006; Dehghanpour, Kempe *et al.*, 2006; Habibi, Lalegani *et al.*, 2007*a*,*b*,*c*; Dehghanpour *et al.*, 2008), the crystal structure of (1) itself has been obtained now for the first time (with the aid of synchrotron radiation because of the very small crystal size and twinning). The analogous Schiff base without nitro groups, *N*,*N*′-bis(*trans*-cinnamaldehyde)ethylenediamine, (3), has previously been crystallographically characterized (Khalaji & Weil, 2007), as have 18 of its complexes with cobalt, nickel, copper, zinc and silver (Meghdadi *et al.*, 2002; Kickelbick *et al.*, 2002, 2003; Khalaji, Aoki & Amirnasr, 2007; Amirnasr *et al.*, 2003, 2006; Khalaji *et al.*, 2006; Khalaji, Amirnasr & Schenk, 2007; Cai *et al.*, 2008). The structures of no other ring-substituted derivatives of this ligand, or complexes of them, have been reported.



(1)



(2)

Scheme 1

2. Experimental

All chemicals were purchased from commercial sources and used as received without further purification. IR spectra were obtained with a Shimadzu IR-435 spectrophotometer using KBr pellets, for the range 4000–400 cm^{-1}. The room-temper-

Table 2
Selected geometric parameters (Å, °) for (1).

C1—C1^{i}	1.528 (5)	C2—N1	1.273 (3)
C1—N1	1.463 (3)		
C1^{i}—C1—N1	109.3 (2)	C1—N1—C2	116.7 (2)
N1—C2—C3—C4	−176.6 (2)	C3—C2—N1—C1	178.9 (2)
C2—C3—C4—C5	179.1 (2)	C1^{i}—C1—N1—C2	125.2 (3)
C3—C4—C5—C6	30.9 (4)	N1^{i}—C1^{i}—C1—N1	180

Symmetry code: (i) $-x+2, -y+1, -z+1$.

ature visible absorption spectra were recorded with a Shimadzu 160 spectrophotometer. NMR spectra were recorded on a Bruker AW 400 MHz spectrometer. Chemical analyses for C, H and N were determined on a Carlo Erba 1108 Elemental Vario EL analyzer.

2.1. Synthesis and crystallization

2.1.1. Synthesis of *N*,*N*′-bis(2-nitrocinnamaldehyde)ethylenediamine, (1). To a solution of ethylenediamine (60 mg, 1 mmol) in methanol (10 ml), cooled in an ice bath, was added dropwise 2-nitrocinnamaldehyde (354 mg, 2 mmol). The mixture was then stirred for an additional 1 h. *N*,*N*′-Bis(2-nitrocinnamaldehyde)ethylenediamine, (1), was obtained as a white microcrystalline precipitate. The precipitate was filtered off and washed with cold absolute methanol (5 ml). The crude product was recrystallized from ethanol to give colourless plate-shaped crystals (yield 340 mg, 90%; m.p. 448–450 K). IR: 1632 cm^{-1} (C═N). ^{1}H NMR ($CDCl_3$): δ 3.91 (*s*, 4H, CH_2—CH_2), 6.89 (*dd*, 2H, N═C—CH), 7.44–7.81 (*m*, 6H, ArH), 7.50 (*d*, 2H, Ar–CH), 8.01 (*d*, 2H, *ortho* to NO_2), 8.78 (*d*, 2H, CH═N). Analysis calculated for $C_{20}H_{18}N_4O_4$: C 63.48, H 4.76, N 14.81%; found: C 63.36, H 4.71, N 14.76%.

2.1.2. Synthesis of [Cu(NCS)(Nca$_2$en)(PPh$_3$)], (2). To a solution of CuNCS (121 mg, 1 mmol) in acetonitrile (5 ml) was added a solution of of PPh_3 (261 mg, 1 mmol) in acetonitrile (5 ml). The mixture was stirred for 5 min and then a solution of Nca$_2$en (378 mg, 1 mmol) in acetonitrile (5 ml) was added and stirring was continued for an additional 60 min. The volume of the solvent was reduced under vacuum to about 5 ml. The diffusion of diethyl ether vapour into the concentrated solution gave orange crystals suitable for X-ray diffraction. The crystals were collected and dried *in vacuo* (yield 611 mg, 80%). IR: 1620 (C═N), 2010 (NCS) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.82 (*s*, 4H$_e$, CH_2–CH_2), 7.21–7.98 (*m*, 27H, Ph—CH═C, C═CH—C, ArH), 8.11 (*d*, 2H, CH═N). Analysis calculated for $C_{39}H_{33}CuN_5O_4PS$: C 61.45, H 4.33, N 9.19%; found: C 61.41, H 4.30, N 9.13%.

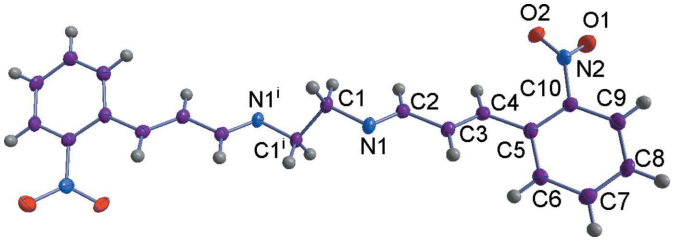


Figure 1
The molecular structure of (1), shown with 50% probability displacement ellipsoids for non-H atoms and spheres of arbitrary size for H atoms. [Symmetry code: (i) $-x+2, -y+1, -z+1$.]

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The small crystal size of (1) necessitated synchrotron data collection at Station 9.8 of the Synchrotron Radiation Source at Daresbury Laboratory. The crystal was a nonmerohedral twin with two components in the ratio 58.0 (2):42.0 (2) related by a 180° rotation around [100]; refinement used both single and overlapped reflections of both components with the HKLF 5 format of *SHELXL2014* (Sheldrick, 2015). Several very strong reflections were rejected because their intensities exceeded the dynamic range of the detector. All H atoms were refined as riding in calculated positions, with ideal geometry and U_{iso}(H) = 1.2U_{eq}(C). In complex (2), the anisotropic displacement parameters suggest that possible disorder may affect one of the nitro groups, but this was not resolved.

3. Results and discussion

3.1. Spectroscopic characterization and coordination of NCS$^-$

IR and NMR spectra of Schiff base (1) and Cu^{I} complex (2) are provided in the *Supporting information*. The IR spectrum of (1) exhibits the characteristic band of an imine group, which appears at 1630 cm^{-1}. This band is shifted to a lower frequency (1620 cm^{-1}) in complex (2) due to the coordination of the imine N atom to copper (Meghdadi *et al.*, 2002). The NCS$^-$ anion can act as either a monodentate or a bridging ligand, leading to the formation of mono- and polynuclear species with different dimensionalities and nuclearities. Having two different donor atoms, NCS$^-$ can coordinate to metal atoms through either the N or the S atom, or both. In agreement with the hard–soft acid–base (HSAB) principle, NCS$^-$ coordinates to hard acids (*e.g.* Mn^{2+}, Co^{2+} and Ni^{2+}) through the N atom and the uncoordinated S atom is involved in hydrogen bonds and/or S···S interactions. If the transition metal centre is a soft acid (*e.g.* Cd^{2+}, Cu^{+} and Hg^{2+}), NCS$^-$ coordinates through the S atom. The mode of coordination of the thiocyanate anion to transition metals is influenced by various factors. These include the electronic and steric effects of ancillary ligands, as well as the solvents used for the synthesis and crystallization of the complexes (Kawaguchi, 1988; Gorji *et al.*, 2001). The coordination of the NCS$^-$ ligand through the N atom to the relatively soft Cu^{+} ion in the case of (2) may be due to the steric limitations imposed by the bulky PPh_3 and Nca$_2$en ligands, and the π-acceptor character of these two ligands. The observation of a strong band at 2070 cm^{-1} and a weak band at 782 cm^{-1} for this complex is assigned to the *N*-coordinated NCS$^-$ ligand in this complex

Table 3
Hydrogen-bond geometry (Å, °) for (1).

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···O2	0.95	2.45	2.788 (3)	101
C4—H4···O2^{ii}	0.95	2.57	3.422 (3)	149
C7—H7···N1^{iii}	0.95	2.61	3.519 (4)	160
C8—H8···O1^{iv}	0.95	2.57	3.458 (4)	155
C9—H9···O1	0.95	2.52	2.769 (3)	95

Symmetry codes: (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x+1, -y+2, -z+1$; (iv) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$.

(Nakamoto, 1992). The ^{1}H NMR data for (1) suggest that the ligand has a symmetrical structure. The four methylene H atoms appear as a singlet at 3.91 p.p.m. The two vinyl C—H hydrogens are observed as a doublet of doublets centred at 6.89 p.p.m., the H atom *ortho* to the nitro group is observed as a doublet at 8.01 p.p.m. and the multiplet at 7.44–7.81 p.p.m. is assigned to the other phenyl H atoms. The two Ar—CH hydrogens are observed as a doublet centred at 7.50 p.p.m. and this is distinguishable from the overlapping multiplet. The two –CH═N hydrogens appear as a doublet at 8.78 p.p.m. The corresponding ^{1}H NMR peak assignments are given in the *Experimental* section for complex (2) (§2.1.2), based on the splitting patterns of the signals and coupling constants in the literature, and are clearly confirmed by the crystallographically determined molecular structure. The proton resonances of the coordinated Nca$_2$en ligand are largely observed at expected positions in the spectrum of the complex. However, the aromatic H atoms of the PPh_3 ligand overlap to some extent with those of the phenyl H atoms of Nca$_2$en. Apart from the aromatic H atoms, which appear at 7.21–7.98 p.p.m., the two imine H atoms appear as a doublet at 8.11 p.p.m. The ethylene H atoms overlap with those of the aromatic region. The downfield shift of the imine H atoms relative to the free ligand can be attributed to the deshielding effect resulting from the coordination of the ligand. The sharp singlet at 3.82 p.p.m. is assigned to the –CH_2—CH_2– H atoms. In the UV–Vis spectrum of Schiff base (1), the aromatic bands at 210–302 nm are attributed to a benzene $\pi\rightarrow\pi^*$ transition. The electronic spectrum of Cu^{I} complex (2) shows an absorption band at 283 nm attributed to the $\pi\rightarrow\pi^*$ transition of the ligand.

3.2. Crystal structure of Nca$_2$en, (1)

The molecular structure of (1) is shown in Fig. 1 and selected bond lengths, bond angles and torsion angles are given in Table 2. The molecule has a *trans* conformation with regard to the central ethylenediamine unit and lies on a crystallographic inversion centre, imposing an N—C—C—N torsion angle of exactly 180°. Each of the C—C═C—C═N—C segments is essentially planar, as expected for an extended conjugation, with all torsion angles close to ±180°, and they are necessarily parallel by crystallographic symmetry, but they are twisted out of the central N—C—C—N plane, with torsion angles of ±125.2 (3)°. They are also somewhat twisted relative to the aromatic rings, a representative torsion angle being 30.9 (4)° for C3—C4—C5—C6, and the dihedral angle between the mean planes of each chain segment and its attached ring being 30.2 (2)°. The other deviation from planarity in the molecular structure is a twist of each nitro group out of the corresponding ring plane, with a dihedral angle of 37.87 (12)°. These twists represent a compromise between repulsive steric interactions of substituents on the one hand, and the extended conjugation afforded by planarity and weak attractive intramolecular C—H···O interactions on the other. There are also some intermolecular C—H···O and C—H···N interactions which may be considered as weak C—H···*X* hydrogen bonds (Table 3). Molecules are stacked along the short crystallographic *b* axis, exhibiting π–π interactions; the centroid–centroid distance between successive parallel aromatic rings is 3.781 (2) Å and the perpendicular interplanar spacing is 3.602 (2) Å.

The bond lengths are typical for C—C and C—N bonds in a conjugated chain, except for the normal central single C—C bond, and the bond angles are also as expected for C and N atoms in such systems. There are no significant differences between this structure and that of the analogue without nitro groups, *i.e.* (3), except that the latter has almost coplanar ring and chain segments within each half of the molecule (Khalaji & Weil, 2007); both have crystallographic inversion symmetry and essentially the same conformation for the conjugated chains and central ethylenediamine unit.

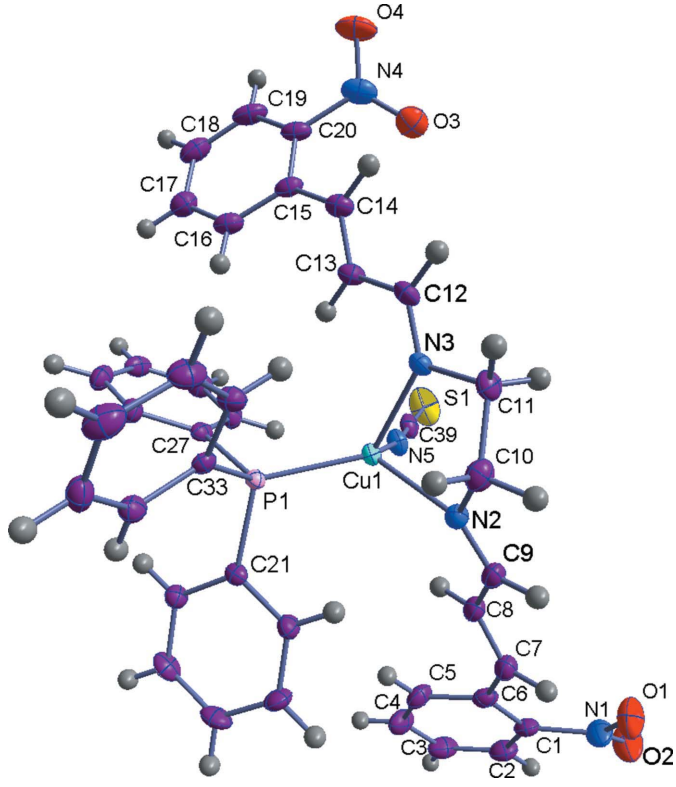


Figure 2
The molecular structure of (2), shown with 50% probability displacement ellipsoids for non-H atoms and spheres of arbitrary size for H atoms. Only the *ipso*-C atoms are labelled in the phenyl rings of the phosphane ligand.

3.3. Crystal structure of [Cu(NCS)(Nca$_2$en)(PPh$_3$)], (2)

The molecular structure of complex (2) is shown in Fig. 2, and selected bond lengths and angles are given in Table 4, with C—H···O and C—H···N interactions listed in Table 5. In this complex, the pseudohalide NCS^- acts as a terminal ligand coordinated through the N atom, and the structure consists of discrete mononuclear molecules containing four-coordinate Cu^I. The bond lengths are normal and the coordination is distorted tetrahedral, the main deviation from ideal tetrahedral geometry being the necessarily restricted N—Cu—N bite angle of 81.56 (12)° for the bidentate ligand forming a five-membered chelate ring; there is only a slight twist of the N2—Cu—N3 and N5—Cu—P1 planes [1.84 (11)°] away from an ideal perpendicular arrangement.

In order to serve as a chelating bidentate ligand to Cu^I, the Schiff base ligand, of course, must change from a *trans* to a *gauche* conformation with regard to the central ethylenediamine unit (somewhat flattened by the small size of the five-membered chelate ring), as indicated by the N—C—C—N torsion angle of 47.6 (4)°. This chelate ring is best described as an envelope, with atom C10 lying 0.625 Å out of the mean plane (r.m.s. deviation = 0.017 Å) of the other four atoms, so the overall conformation of the ligand is somewhat unsymmetrical (a symmetrical arrangement would give a chelate ring twisted on the C—C bond). This asymmetry can be seen in the difference of 30° in the respective torsion angles around the N—C bonds (Table 4), but it does not significantly extend outwards to the conjugated chain segments and aromatic rings; each of these consists of an essentially planar chain twisted by around 35° relative to its attached ring, similar to the twist found in the uncomplexed ligand. In complex (2), as in its uncomplexed state, *i.e.* (1), the ligand shows a twist of the nitro groups out of the ring planes, with dihedral angles of 9.8 (3) and 32.39 (13)°, *i.e.* one smaller than and the other similar to that found in (1). Here too the deviations from planarity are a compromise between steric and electronic factors; weak C—H···O and C—H···N interactions, both intra- and intermolecular, are listed in Table 5. An additional significant intermolecular interaction in the complex is a ring-stacking interaction between inversion-related C1–C6 rings, with a centroid–centroid distance of 3.653 (3) Å and a perpendicular interplanar distance of 3.535 (2) Å. Overall, Nca$_2$en has a rather more bowed shape in the complex than in its own crystal structure.

In metal complexes of Schiff bases (1) and (3), there is some variation in the conformation of the chelate ring, with no obvious pattern or clear indication of specific factors favouring envelope or twist forms. Apart from this particular feature, the bond lengths and angles within the ligands in these complexes remain essentially constant (discounting a small number of outliers, which are likely to be a consequence of reported or unresolved disorder), while there is a range of deviations from planarity of the conjugated chain–ring–nitro units. For the 14 previously reported tetrahedral copper complexes of (1) (six complexes) (Habibi, Lalegani *et al.*, 2007*a*; Kickelbick *et al.*, 2002, 2003) and (3) (eight complexes) (Habibi, Montazerozohori *et al.*, 2007; Dehghanpour, Kempe *et al.*, 2006; Habibi, Lalegani *et al.*, 2007*a*,*b*,*c*; Kickelbick *et al.*, 2002), the range of Cu—N bond lengths is 2.009–2.127 Å, with a mean of 2.079 Å, which compares well with the distances of 2.109 (3) and 2.067 (3) Å in Cu^I complex (2).

Table 4
Selected geometric parameters (Å, °) for (2).

Cu1—N2	2.109 (3)	N3—C11	1.471 (5)
Cu1—N3	2.067 (3)	N3—C12	1.273 (5)
Cu1—P1	2.2049 (10)	C10—C11	1.522 (5)
Cu1—N5	1.973 (3)	N5—C39	1.151 (5)
N2—C9	1.272 (5)	C39—S1	1.629 (4)
N2—C10	1.465 (5)		
N2—Cu1—N3	81.56 (12)	C9—N2—C10	119.7 (3)
N2—Cu1—P1	118.76 (9)	Cu1—N3—C11	112.5 (2)
N2—Cu1—N5	110.10 (13)	Cu1—N3—C12	129.1 (3)
N3—Cu1—P1	117.58 (9)	C11—N3—C12	118.2 (3)
N3—Cu1—N5	105.80 (12)	N2—C10—C11	109.1 (3)
P1—Cu1—N5	117.29 (9)	N3—C11—C10	109.3 (3)
Cu1—N2—C9	134.3 (3)	Cu1—N5—C39	168.7 (3)
Cu1—N2—C10	106.0 (2)	N5—C39—S1	179.0 (4)
C5—C6—C7—C8	−37.4 (6)	N2—C10—C11—N3	47.6 (4)
C6—C7—C8—C9	175.6 (4)	C11—N3—C12—C13	176.9 (3)
C10—N2—C9—C8	179.4 (3)	N3—C12—C13—C14	−178.9 (4)
C7—C8—C9—N2	−174.9 (4)	C12—C13—C14—C15	−177.0 (4)
C9—N2—C10—C11	130.6 (4)	C13—C14—C15—C16	34.2 (6)
C12—N3—C11—C10	161.0 (3)		

Table 5
Hydrogen-bond geometry (Å, °) for (2).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O2	0.95	2.31	2.640 (6)	100
C7—H7···O1	0.95	2.28	2.735 (5)	109
C7—H7···O3^{i}	0.95	2.54	3.468 (5)	165
C11—H11*B*···N5^{i}	0.99	2.59	3.339 (5)	133
C14—H14···O3	0.95	2.44	2.757 (5)	99
C14—H14···O1^{i}	0.95	2.48	3.387 (5)	159
C19—H19···O4	0.95	2.51	2.757 (6)	95
C24—H24···O2^{ii}	0.95	2.62	3.297 (6)	129
C28—H28···N5	0.95	2.61	3.471 (5)	151

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+2, -y, -z+1$.

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Synthesis, characterization and crystal structures of the bidentate Schiff base *N*,*N*′-bis(2-nitrocinnamaldehyde)ethylenediamine and its complex with CuNCS and triphenylphosphane

William Clegg, Ross W. Harrington, Kazem Barati, Mohammad Hossein Habibi, Morteza Montazerozohori and Arash Lalegani

Computing details

Data collection: *APEX2* (Bruker, 2006) for (1); *SMART* (Bruker, 2006) for (2). Cell refinement: *APEX2* (Bruker, 2006) for (1); *SAINT* (Bruker, 2006) for (2). Data reduction: *APEX2* (Bruker, 2006) for (1); *SAINT* (Bruker, 2006) for (2). For both compounds, program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008b); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2012). Software used to prepare material for publication: *SHELXL2014*/7 (Sheldrick, 2015) and local programs for (1); *SHELXL2014* (Sheldrick, 2015) and local programs for (2).

(1) (*E*,*E*)-*N*,*N*′-Bis[(*E*)-3-(2-nitrophenyl)prop-2-en-1-ylidene]ethane-1,2-diamine

Crystal data

$C_{20}H_{18}N_4O_4$
M_r = 378.38
Monoclinic, $P2_1/n$
a = 11.441 (7) Å
b = 3.781 (2) Å
c = 20.553 (12) Å
β = 97.444 (10)°
V = 881.6 (9) Å^3
Z = 2
$F(000)$ = 396
D_x = 1.425 Mg m^{-3}
Synchrotron radiation, λ = 0.6727 Å
Cell parameters from 667 reflections
θ = 3.8–24.9°
μ = 0.10 mm^{-1}
T = 120 K
Plate, colourless
0.10 × 0.08 × 0.01 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: Daresbury SRS station 9.8
thin–slice ω scans
Absorption correction: multi-scan (TWINABS; Sheldrick, 2008a)
T_{min} = 0.90, T_{max} = 1.00
8304 measured reflections
3085 independent reflections
2804 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 24.9°, θ_{min} = 3.8°
h = −14→14
k = −4→4
l = −25→25

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.125$
$S = 0.97$
3085 reflections
128 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0714P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refined as a 2-component twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.9926 (2)	0.5701 (7)	0.53409 (11)	0.0227 (6)
H1A	1.0109	0.3807	0.5671	0.027*
H1B	1.0479	0.7686	0.5456	0.027*
C2	0.8147 (2)	0.5585 (6)	0.57802 (11)	0.0216 (5)
H2	0.8516	0.3868	0.6076	0.026*
C3	0.6941 (2)	0.6670 (6)	0.58311 (11)	0.0216 (5)
H3	0.6570	0.8293	0.5517	0.026*
C4	0.6331 (2)	0.5488 (6)	0.62995 (11)	0.0207 (6)
H4	0.6704	0.3840	0.6608	0.025*
C5	0.5119 (2)	0.6585 (6)	0.63654 (11)	0.0205 (6)
C6	0.4326 (2)	0.7507 (6)	0.58151 (11)	0.0230 (6)
H6	0.4586	0.7426	0.5395	0.028*
C7	0.3179 (2)	0.8534 (7)	0.58595 (12)	0.0249 (6)
H7	0.2672	0.9197	0.5476	0.030*
C8	0.2772 (2)	0.8591 (7)	0.64661 (11)	0.0248 (6)
H8	0.1985	0.9302	0.6499	0.030*
C9	0.3508 (2)	0.7616 (7)	0.70205 (12)	0.0241 (6)
H9	0.3229	0.7601	0.7436	0.029*
C10	0.4660 (2)	0.6657 (6)	0.69655 (11)	0.0209 (6)
N1	0.87125 (19)	0.6910 (6)	0.53446 (9)	0.0219 (5)
N2	0.5416 (2)	0.5838 (6)	0.75785 (10)	0.0263 (5)
O1	0.49714 (18)	0.4252 (6)	0.80087 (8)	0.0371 (5)
O2	0.64449 (17)	0.6823 (6)	0.76401 (8)	0.0362 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0171 (13)	0.0241 (13)	0.0275 (13)	0.0013 (11)	0.0055 (11)	0.0015 (10)

C2	0.0213 (13)	0.0208 (13)	0.0223 (12)	0.0015 (11)	0.0017 (11)	−0.0025 (10)
C3	0.0207 (14)	0.0212 (13)	0.0228 (11)	0.0016 (11)	0.0027 (10)	−0.0005 (10)
C4	0.0186 (14)	0.0210 (13)	0.0218 (12)	0.0007 (11)	0.0006 (10)	−0.0017 (10)
C5	0.0209 (14)	0.0168 (13)	0.0244 (12)	−0.0023 (11)	0.0054 (11)	−0.0011 (9)
C6	0.0232 (14)	0.0232 (14)	0.0233 (12)	−0.0018 (11)	0.0053 (12)	−0.0005 (10)
C7	0.0205 (14)	0.0270 (14)	0.0267 (12)	−0.0007 (13)	0.0016 (11)	0.0021 (11)
C8	0.0156 (13)	0.0262 (15)	0.0332 (13)	0.0016 (11)	0.0054 (11)	−0.0003 (11)
C9	0.0203 (14)	0.0288 (14)	0.0245 (12)	−0.0045 (12)	0.0084 (11)	−0.0008 (11)
C10	0.0203 (14)	0.0206 (14)	0.0213 (11)	−0.0027 (11)	0.0010 (11)	−0.0006 (10)
N1	0.0176 (11)	0.0247 (11)	0.0241 (10)	0.0012 (9)	0.0053 (9)	−0.0012 (9)
N2	0.0209 (12)	0.0350 (13)	0.0238 (11)	0.0026 (10)	0.0061 (10)	−0.0022 (9)
O1	0.0322 (12)	0.0533 (13)	0.0270 (9)	0.0045 (11)	0.0087 (9)	0.0126 (9)
O2	0.0169 (10)	0.0620 (14)	0.0295 (9)	−0.0023 (10)	0.0018 (8)	−0.0076 (9)

Geometric parameters (Å, º)

C1—C1^{i}	1.528 (5)	C5—C10	1.402 (3)
C1—H1A	0.990	C6—H6	0.950
C1—H1B	0.990	C6—C7	1.383 (4)
C1—N1	1.463 (3)	C7—H7	0.950
C2—H2	0.950	C7—C8	1.386 (3)
C2—C3	1.456 (4)	C8—H8	0.950
C2—N1	1.273 (3)	C8—C9	1.376 (4)
C3—H3	0.950	C9—H9	0.950
C3—C4	1.337 (3)	C9—C10	1.386 (4)
C4—H4	0.950	C10—N2	1.466 (3)
C4—C5	1.471 (3)	N2—O1	1.232 (3)
C5—C6	1.399 (3)	N2—O2	1.225 (3)
C1^{i}—C1—H1A	109.8	C5—C6—C7	122.5 (2)
C1^{i}—C1—H1B	109.8	H6—C6—C7	118.7
C1^{i}—C1—N1	109.3 (2)	C6—C7—H7	120.1
H1A—C1—H1B	108.3	C6—C7—C8	119.7 (2)
H1A—C1—N1	109.8	H7—C7—C8	120.1
H1B—C1—N1	109.8	C7—C8—H8	120.0
H2—C2—C3	119.6	C7—C8—C9	120.0 (3)
H2—C2—N1	119.6	H8—C8—C9	120.0
C3—C2—N1	120.8 (2)	C8—C9—H9	120.4
C2—C3—H3	118.5	C8—C9—C10	119.3 (2)
C2—C3—C4	123.0 (2)	H9—C9—C10	120.4
H3—C3—C4	118.5	C5—C10—C9	123.0 (2)
C3—C4—H4	118.0	C5—C10—N2	120.4 (2)
C3—C4—C5	123.9 (2)	C9—C10—N2	116.5 (2)
H4—C4—C5	118.0	C1—N1—C2	116.7 (2)
C4—C5—C6	121.1 (2)	C10—N2—O1	117.8 (2)
C4—C5—C10	123.5 (2)	C10—N2—O2	118.5 (2)
C6—C5—C10	115.4 (2)	O1—N2—O2	123.7 (2)
C5—C6—H6	118.7		

N1—C2—C3—C4	−176.6 (2)	C4—C5—C10—C9	−178.4 (2)
C2—C3—C4—C5	179.1 (2)	C4—C5—C10—N2	4.1 (4)
C3—C4—C5—C6	30.9 (4)	C6—C5—C10—C9	−0.9 (4)
C3—C4—C5—C10	−151.6 (2)	C6—C5—C10—N2	−178.3 (2)
C4—C5—C6—C7	179.7 (2)	C3—C2—N1—C1	178.9 (2)
C10—C5—C6—C7	2.0 (4)	C1^{i}—C1—N1—C2	125.2 (3)
C5—C6—C7—C8	−1.5 (4)	C5—C10—N2—O1	−144.7 (2)
C6—C7—C8—C9	−0.2 (4)	C5—C10—N2—O2	36.7 (3)
C7—C8—C9—C10	1.4 (4)	C9—C10—N2—O1	37.7 (3)
C8—C9—C10—C5	−0.8 (4)	C9—C10—N2—O2	−140.9 (2)
C8—C9—C10—N2	176.7 (2)	N1^{i}—C1^{i}—C1—N1	180

Symmetry code: (i) −*x*+2, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O2	0.95	2.45	2.788 (3)	101
C4—H4···O2^{ii}	0.95	2.57	3.422 (3)	149
C7—H7···N1^{iii}	0.95	2.61	3.519 (4)	160
C8—H8···O1^{iv}	0.95	2.57	3.458 (4)	155
C9—H9···O1	0.95	2.52	2.769 (3)	95

Symmetry codes: (ii) −*x*+3/2, *y*−1/2, −*z*+3/2; (iii) −*x*+1, −*y*+2, −*z*+1; (iv) −*x*+1/2, *y*+1/2, −*z*+3/2.

(2) {(1*E*,1′*E*,2*E*,2′*E*)-*N*,*N*′-(Ethane-1,2-diyl)bis[3-(2-nitrophenyl)prop-2-en-1-imine]-κ^2*N*,*N*′}(thiocyanato-κ*N*)(triphenylphosphane-κ*P*)copper(I)]

Crystal data

[Cu(NCS)($C_{20}H_{18}N_4O_4$)($C_{18}H_{15}P$)]
M_r = 762.27
Triclinic, $P\overline{1}$
a = 9.1038 (8) Å
b = 13.8186 (12) Å
c = 15.2972 (14) Å
α = 104.7831 (14)°
β = 102.6778 (14)°
γ = 91.3000 (14)°
V = 1809.0 (3) Å^3

Z = 2
F(000) = 788
D_x = 1.399 Mg m^{-3}
Mo *K*α radiation, λ = 0.71073 Å
Cell parameters from 5264 reflections
θ = 2.3–26.3°
μ = 0.75 mm^{-1}
T = 150 K
Block, orange
0.34 × 0.30 × 0.30 mm

Data collection

Bruker SMART 1K CCD diffractometer
Radiation source: sealed tube
thin–slice ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008a)
T_{min} = 0.75, T_{max} = 0.81
14710 measured reflections

7308 independent reflections
6786 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 26.4°, θ_{min} = 1.5°
h = −11→11
k = −17→17
l = −19→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.130$
$S = 1.35$
7308 reflections
460 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0213P)^2 + 4.1072P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.76$ e Å^{-3}
$\Delta\rho_{min} = -0.65$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.43497 (5)	0.33281 (3)	0.31978 (3)	0.01539 (12)
N1	1.1164 (4)	0.1899 (3)	0.6447 (3)	0.0363 (9)
O1	1.0179 (4)	0.2216 (3)	0.6828 (2)	0.0429 (8)
O2	1.2495 (5)	0.1992 (4)	0.6860 (3)	0.0940 (19)
N2	0.4633 (4)	0.3011 (2)	0.4500 (2)	0.0206 (7)
O3	0.2966 (4)	0.8025 (2)	0.2733 (2)	0.0371 (7)
O4	0.1522 (4)	0.8761 (2)	0.1817 (3)	0.0429 (8)
N3	0.3104 (3)	0.4428 (2)	0.3803 (2)	0.0177 (6)
N4	0.2166 (4)	0.8030 (3)	0.1977 (3)	0.0306 (8)
C1	1.0814 (5)	0.1430 (3)	0.5439 (3)	0.0248 (8)
C2	1.1994 (5)	0.0993 (3)	0.5090 (3)	0.0311 (9)
H2	1.2956	0.1016	0.5495	0.037*
C3	1.1776 (5)	0.0526 (3)	0.4158 (3)	0.0342 (10)
H3	1.2576	0.0215	0.3916	0.041*
C4	1.0375 (5)	0.0515 (3)	0.3578 (3)	0.0351 (10)
H4	1.0210	0.0195	0.2932	0.042*
C5	0.9209 (5)	0.0968 (3)	0.3930 (3)	0.0290 (9)
H5	0.8260	0.0958	0.3516	0.035*
C6	0.9384 (4)	0.1440 (3)	0.4876 (3)	0.0241 (8)
C7	0.8048 (4)	0.1859 (3)	0.5189 (3)	0.0241 (8)
H7	0.7916	0.1806	0.5774	0.029*
C8	0.7016 (4)	0.2309 (3)	0.4697 (3)	0.0234 (8)
H8	0.7172	0.2410	0.4132	0.028*
C9	0.5667 (4)	0.2648 (3)	0.4997 (3)	0.0230 (8)
H9	0.5550	0.2597	0.5586	0.028*

C10	0.3289 (4)	0.3330 (3)	0.4839 (3)	0.0250 (8)
H10A	0.3443	0.3328	0.5500	0.030*
H10B	0.2402	0.2858	0.4475	0.030*
C11	0.3008 (5)	0.4383 (3)	0.4740 (3)	0.0244 (8)
H11A	0.1995	0.4550	0.4839	0.029*
H11B	0.3771	0.4878	0.5213	0.029*
C12	0.2507 (4)	0.5137 (3)	0.3497 (3)	0.0211 (8)
H12	0.1976	0.5593	0.3867	0.025*
C13	0.2612 (4)	0.5268 (3)	0.2607 (3)	0.0224 (8)
H13	0.3127	0.4804	0.2233	0.027*
C14	0.2011 (4)	0.6016 (3)	0.2294 (3)	0.0228 (8)
H14	0.1545	0.6487	0.2695	0.027*
C15	0.2005 (4)	0.6177 (3)	0.1380 (3)	0.0227 (8)
C16	0.1887 (4)	0.5350 (3)	0.0609 (3)	0.0275 (9)
H16	0.1907	0.4694	0.0698	0.033*
C17	0.1742 (5)	0.5464 (3)	−0.0282 (3)	0.0303 (9)
H17	0.1672	0.4891	−0.0792	0.036*
C18	0.1698 (5)	0.6411 (4)	−0.0425 (3)	0.0338 (10)
H18	0.1583	0.6486	−0.1036	0.041*
C19	0.1820 (5)	0.7246 (3)	0.0312 (3)	0.0325 (10)
H19	0.1798	0.7899	0.0216	0.039*
C20	0.1974 (4)	0.7119 (3)	0.1196 (3)	0.0254 (8)
P1	0.31569 (10)	0.21748 (6)	0.19398 (6)	0.01374 (19)
C21	0.3989 (4)	0.0974 (3)	0.1825 (2)	0.0152 (7)
C22	0.4603 (4)	0.0721 (3)	0.2646 (3)	0.0204 (8)
H22	0.4588	0.1177	0.3225	0.025*
C23	0.5239 (4)	−0.0185 (3)	0.2633 (3)	0.0268 (9)
H23	0.5651	−0.0348	0.3199	0.032*
C24	0.5267 (4)	−0.0849 (3)	0.1791 (3)	0.0281 (9)
H24	0.5708	−0.1467	0.1779	0.034*
C25	0.4658 (4)	−0.0616 (3)	0.0971 (3)	0.0249 (8)
H25	0.4668	−0.1078	0.0394	0.030*
C26	0.4026 (4)	0.0294 (3)	0.0985 (3)	0.0193 (7)
H26	0.3617	0.0452	0.0416	0.023*
C27	0.3137 (4)	0.2494 (3)	0.0845 (2)	0.0165 (7)
C28	0.4350 (4)	0.3106 (3)	0.0812 (3)	0.0224 (8)
H28	0.5170	0.3320	0.1341	0.027*
C29	0.4374 (4)	0.3407 (3)	0.0016 (3)	0.0259 (8)
H29	0.5204	0.3831	0.0006	0.031*
C30	0.3196 (4)	0.3093 (3)	−0.0762 (3)	0.0254 (8)
H30	0.3213	0.3300	−0.1307	0.030*
C31	0.1996 (4)	0.2479 (3)	−0.0743 (3)	0.0256 (8)
H31	0.1193	0.2251	−0.1280	0.031*
C32	0.1955 (4)	0.2192 (3)	0.0058 (3)	0.0213 (8)
H32	0.1109	0.1784	0.0069	0.026*
C33	0.1166 (4)	0.1808 (3)	0.1830 (2)	0.0155 (7)
C34	0.0477 (4)	0.0854 (3)	0.1332 (3)	0.0203 (8)
H34	0.1052	0.0361	0.1039	0.024*

C35	−0.1039 (4)	0.0623 (3)	0.1264 (3)	0.0261 (9)
H35	−0.1498	−0.0029	0.0929	0.031*
C36	−0.1894 (5)	0.1347 (3)	0.1684 (3)	0.0303 (9)
H36	−0.2941	0.1196	0.1622	0.036*
C37	−0.1212 (4)	0.2277 (3)	0.2188 (3)	0.0255 (8)
H37	−0.1785	0.2763	0.2491	0.031*
C38	0.0300 (4)	0.2514 (3)	0.2260 (3)	0.0199 (8)
H38	0.0754	0.3165	0.2606	0.024*
N5	0.6208 (4)	0.4041 (2)	0.3132 (2)	0.0232 (7)
C39	0.7137 (4)	0.4576 (3)	0.3062 (3)	0.0245 (8)
S1	0.84730 (16)	0.53232 (11)	0.29704 (10)	0.0519 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0173 (2)	0.0141 (2)	0.0127 (2)	0.00109 (16)	0.00241 (16)	0.00084 (16)
N1	0.039 (2)	0.036 (2)	0.0279 (19)	0.0180 (17)	−0.0045 (17)	0.0070 (16)
O1	0.0356 (18)	0.061 (2)	0.0277 (17)	0.0044 (16)	0.0083 (14)	0.0030 (15)
O2	0.062 (3)	0.140 (5)	0.047 (2)	0.061 (3)	−0.017 (2)	−0.013 (3)
N2	0.0249 (16)	0.0189 (15)	0.0177 (15)	0.0019 (13)	0.0046 (13)	0.0047 (12)
O3	0.0451 (19)	0.0303 (16)	0.0408 (19)	0.0021 (14)	0.0158 (16)	0.0134 (14)
O4	0.0435 (19)	0.0250 (16)	0.071 (2)	0.0142 (14)	0.0235 (17)	0.0219 (16)
N3	0.0194 (15)	0.0146 (14)	0.0187 (15)	0.0028 (12)	0.0056 (12)	0.0025 (12)
N4	0.0294 (19)	0.0238 (18)	0.049 (2)	0.0043 (15)	0.0212 (18)	0.0174 (16)
C1	0.029 (2)	0.0224 (19)	0.026 (2)	0.0082 (16)	0.0051 (17)	0.0117 (16)
C2	0.030 (2)	0.031 (2)	0.038 (2)	0.0086 (18)	0.0086 (19)	0.0176 (19)
C3	0.041 (3)	0.035 (2)	0.041 (3)	0.017 (2)	0.025 (2)	0.020 (2)
C4	0.052 (3)	0.039 (2)	0.022 (2)	0.014 (2)	0.019 (2)	0.0135 (19)
C5	0.033 (2)	0.037 (2)	0.022 (2)	0.0062 (18)	0.0069 (17)	0.0161 (18)
C6	0.030 (2)	0.0219 (19)	0.025 (2)	0.0037 (16)	0.0072 (17)	0.0139 (16)
C7	0.028 (2)	0.026 (2)	0.0189 (19)	0.0023 (16)	0.0053 (16)	0.0071 (16)
C8	0.025 (2)	0.026 (2)	0.0177 (18)	0.0013 (16)	0.0007 (15)	0.0067 (15)
C9	0.030 (2)	0.0215 (19)	0.0175 (18)	0.0010 (16)	0.0047 (16)	0.0067 (15)
C10	0.028 (2)	0.031 (2)	0.0198 (19)	0.0021 (17)	0.0085 (16)	0.0106 (16)
C11	0.028 (2)	0.028 (2)	0.0181 (19)	0.0069 (17)	0.0101 (16)	0.0036 (16)
C12	0.0225 (19)	0.0156 (17)	0.0227 (19)	0.0000 (15)	0.0071 (15)	−0.0010 (14)
C13	0.0226 (19)	0.0203 (19)	0.027 (2)	0.0065 (15)	0.0094 (16)	0.0069 (15)
C14	0.0203 (19)	0.0177 (18)	0.032 (2)	0.0037 (15)	0.0094 (16)	0.0068 (16)
C15	0.0173 (18)	0.025 (2)	0.030 (2)	0.0062 (15)	0.0073 (16)	0.0128 (16)
C16	0.023 (2)	0.026 (2)	0.037 (2)	0.0080 (16)	0.0078 (18)	0.0148 (18)
C17	0.026 (2)	0.036 (2)	0.030 (2)	0.0058 (18)	0.0046 (18)	0.0122 (19)
C18	0.027 (2)	0.050 (3)	0.034 (2)	0.012 (2)	0.0094 (19)	0.024 (2)
C19	0.026 (2)	0.035 (2)	0.049 (3)	0.0113 (18)	0.013 (2)	0.027 (2)
C20	0.0186 (19)	0.024 (2)	0.039 (2)	0.0076 (16)	0.0103 (17)	0.0142 (17)
P1	0.0133 (4)	0.0131 (4)	0.0143 (4)	0.0019 (3)	0.0034 (3)	0.0025 (3)
C21	0.0091 (15)	0.0145 (16)	0.0218 (18)	0.0012 (13)	0.0048 (14)	0.0034 (14)
C22	0.0216 (18)	0.0207 (18)	0.0185 (18)	0.0034 (15)	0.0047 (15)	0.0041 (15)
C23	0.027 (2)	0.026 (2)	0.029 (2)	0.0074 (17)	0.0001 (17)	0.0146 (17)

C24	0.026 (2)	0.0162 (18)	0.044 (3)	0.0082 (16)	0.0129 (19)	0.0075 (17)
C25	0.028 (2)	0.0206 (19)	0.027 (2)	0.0019 (16)	0.0169 (17)	−0.0016 (16)
C26	0.0183 (18)	0.0206 (18)	0.0191 (18)	0.0035 (14)	0.0062 (15)	0.0036 (14)
C27	0.0178 (17)	0.0181 (17)	0.0138 (17)	0.0051 (14)	0.0049 (14)	0.0031 (14)
C28	0.0219 (19)	0.026 (2)	0.0174 (18)	0.0015 (16)	0.0031 (15)	0.0046 (15)
C29	0.024 (2)	0.028 (2)	0.030 (2)	0.0008 (16)	0.0127 (17)	0.0101 (17)
C30	0.030 (2)	0.030 (2)	0.0212 (19)	0.0132 (17)	0.0126 (17)	0.0109 (16)
C31	0.023 (2)	0.035 (2)	0.0173 (19)	0.0056 (17)	0.0020 (16)	0.0065 (16)
C32	0.0185 (18)	0.0231 (19)	0.0218 (19)	0.0020 (15)	0.0036 (15)	0.0060 (15)
C33	0.0140 (16)	0.0172 (17)	0.0166 (17)	0.0007 (14)	0.0028 (14)	0.0076 (14)
C34	0.0181 (18)	0.0226 (19)	0.0211 (19)	0.0032 (15)	0.0058 (15)	0.0059 (15)
C35	0.023 (2)	0.028 (2)	0.023 (2)	−0.0063 (16)	−0.0011 (16)	0.0062 (16)
C36	0.0188 (19)	0.037 (2)	0.041 (3)	0.0043 (17)	0.0090 (18)	0.019 (2)
C37	0.0221 (19)	0.029 (2)	0.029 (2)	0.0092 (16)	0.0111 (17)	0.0095 (17)
C38	0.0185 (18)	0.0181 (18)	0.0250 (19)	0.0040 (14)	0.0078 (15)	0.0067 (15)
N5	0.0208 (16)	0.0238 (17)	0.0216 (17)	−0.0042 (14)	0.0055 (13)	−0.0001 (13)
C39	0.024 (2)	0.028 (2)	0.0189 (19)	0.0036 (17)	0.0079 (16)	−0.0015 (16)
S1	0.0490 (8)	0.0519 (8)	0.0543 (8)	−0.0218 (6)	0.0266 (7)	0.0030 (6)

Geometric parameters (Å, º)

Cu1—N2	2.109 (3)	C17—H17	0.950
Cu1—N3	2.067 (3)	C17—C18	1.380 (6)
Cu1—P1	2.2049 (10)	C18—H18	0.950
Cu1—N5	1.973 (3)	C18—C19	1.374 (6)
N1—O1	1.205 (5)	C19—H19	0.950
N1—O2	1.225 (5)	C19—C20	1.386 (6)
N1—C1	1.471 (5)	P1—C21	1.824 (3)
N2—C9	1.272 (5)	P1—C27	1.834 (4)
N2—C10	1.465 (5)	P1—C33	1.831 (3)
O3—N4	1.225 (5)	C21—C22	1.391 (5)
O4—N4	1.230 (4)	C21—C26	1.393 (5)
N3—C11	1.471 (5)	C22—H22	0.950
N3—C12	1.273 (5)	C22—C23	1.389 (5)
N4—C20	1.474 (5)	C23—H23	0.950
C1—C2	1.386 (6)	C23—C24	1.383 (6)
C1—C6	1.398 (5)	C24—H24	0.950
C2—H2	0.950	C24—C25	1.376 (6)
C2—C3	1.374 (6)	C25—H25	0.950
C3—H3	0.950	C25—C26	1.391 (5)
C3—C4	1.383 (6)	C26—H26	0.950
C4—H4	0.950	C27—C28	1.393 (5)
C4—C5	1.385 (6)	C27—C32	1.391 (5)
C5—H5	0.950	C28—H28	0.950
C5—C6	1.399 (6)	C28—C29	1.389 (5)
C6—C7	1.479 (5)	C29—H29	0.950
C7—H7	0.950	C29—C30	1.383 (6)
C7—C8	1.338 (5)	C30—H30	0.950

C8—H8	0.950	C30—C31	1.378 (6)
C8—C9	1.449 (5)	C31—H31	0.950
C9—H9	0.950	C31—C32	1.388 (5)
C10—H10A	0.990	C32—H32	0.950
C10—H10B	0.990	C33—C34	1.397 (5)
C10—C11	1.522 (5)	C33—C38	1.393 (5)
C11—H11A	0.990	C34—H34	0.950
C11—H11B	0.990	C34—C35	1.385 (5)
C12—H12	0.950	C35—H35	0.950
C12—C13	1.442 (5)	C35—C36	1.395 (6)
C13—H13	0.950	C36—H36	0.950
C13—C14	1.326 (5)	C36—C37	1.371 (6)
C14—H14	0.950	C37—H37	0.950
C14—C15	1.470 (5)	C37—C38	1.382 (5)
C15—C16	1.400 (6)	C38—H38	0.950
C15—C20	1.399 (5)	N5—C39	1.151 (5)
C16—H16	0.950	C39—S1	1.629 (4)
C16—C17	1.390 (6)		

N2—Cu1—N3	81.56 (12)	C16—C17—C18	120.0 (4)
N2—Cu1—P1	118.76 (9)	H17—C17—C18	120.0
N2—Cu1—N5	110.10 (13)	C17—C18—H18	119.8
N3—Cu1—P1	117.58 (9)	C17—C18—C19	120.4 (4)
N3—Cu1—N5	105.80 (12)	H18—C18—C19	119.8
P1—Cu1—N5	117.29 (9)	C18—C19—H19	120.6
O1—N1—O2	122.5 (4)	C18—C19—C20	118.8 (4)
O1—N1—C1	120.5 (4)	H19—C19—C20	120.6
O2—N1—C1	116.9 (4)	N4—C20—C15	119.2 (4)
Cu1—N2—C9	134.3 (3)	N4—C20—C19	117.6 (4)
Cu1—N2—C10	106.0 (2)	C15—C20—C19	123.2 (4)
C9—N2—C10	119.7 (3)	Cu1—P1—C21	112.49 (11)
Cu1—N3—C11	112.5 (2)	Cu1—P1—C27	114.52 (12)
Cu1—N3—C12	129.1 (3)	Cu1—P1—C33	118.05 (12)
C11—N3—C12	118.2 (3)	C21—P1—C27	105.11 (16)
O3—N4—O4	124.0 (4)	C21—P1—C33	102.08 (15)
O3—N4—C20	118.9 (3)	C27—P1—C33	103.01 (16)
O4—N4—C20	117.1 (4)	P1—C21—C22	116.6 (3)
N1—C1—C2	115.7 (4)	P1—C21—C26	125.0 (3)
N1—C1—C6	121.6 (4)	C22—C21—C26	118.3 (3)
C2—C1—C6	122.6 (4)	C21—C22—H22	119.4
C1—C2—H2	119.9	C21—C22—C23	121.1 (3)
C1—C2—C3	120.2 (4)	H22—C22—C23	119.4
H2—C2—C3	119.9	C22—C23—H23	120.2
C2—C3—H3	120.5	C22—C23—C24	119.6 (4)
C2—C3—C4	119.0 (4)	H23—C23—C24	120.2
H3—C3—C4	120.5	C23—C24—H24	119.9
C3—C4—H4	119.7	C23—C24—C25	120.2 (3)
C3—C4—C5	120.5 (4)	H24—C24—C25	119.9

H4—C4—C5	119.7	C24—C25—H25	119.9
C4—C5—H5	118.9	C24—C25—C26	120.1 (3)
C4—C5—C6	122.1 (4)	H25—C25—C26	119.9
H5—C5—C6	118.9	C21—C26—C25	120.6 (3)
C1—C6—C5	115.6 (4)	C21—C26—H26	119.7
C1—C6—C7	126.5 (4)	C25—C26—H26	119.7
C5—C6—C7	117.9 (4)	P1—C27—C28	118.0 (3)
C6—C7—H7	118.0	P1—C27—C32	123.8 (3)
C6—C7—C8	124.0 (4)	C28—C27—C32	118.2 (3)
H7—C7—C8	118.0	C27—C28—H28	119.6
C7—C8—H8	118.8	C27—C28—C29	120.8 (3)
C7—C8—C9	122.4 (4)	H28—C28—C29	119.6
H8—C8—C9	118.8	C28—C29—H29	119.9
N2—C9—C8	122.4 (3)	C28—C29—C30	120.2 (4)
N2—C9—H9	118.8	H29—C29—C30	119.9
C8—C9—H9	118.8	C29—C30—H30	120.2
N2—C10—H10A	109.9	C29—C30—C31	119.6 (4)
N2—C10—H10B	109.9	H30—C30—C31	120.2
N2—C10—C11	109.1 (3)	C30—C31—H31	119.9
H10A—C10—H10B	108.3	C30—C31—C32	120.3 (4)
H10A—C10—C11	109.9	H31—C31—C32	119.9
H10B—C10—C11	109.9	C27—C32—C31	120.9 (4)
N3—C11—C10	109.3 (3)	C27—C32—H32	119.6
N3—C11—H11A	109.8	C31—C32—H32	119.6
N3—C11—H11B	109.8	P1—C33—C34	122.9 (3)
C10—C11—H11A	109.8	P1—C33—C38	118.4 (3)
C10—C11—H11B	109.8	C34—C33—C38	118.7 (3)
H11A—C11—H11B	108.3	C33—C34—H34	119.8
N3—C12—H12	119.0	C33—C34—C35	120.3 (3)
N3—C12—C13	122.0 (3)	H34—C34—C35	119.8
H12—C12—C13	119.0	C34—C35—H35	119.9
C12—C13—H13	119.0	C34—C35—C36	120.1 (4)
C12—C13—C14	122.0 (4)	H35—C35—C36	119.9
H13—C13—C14	119.0	C35—C36—H36	120.2
C13—C14—H14	117.2	C35—C36—C37	119.5 (4)
C13—C14—C15	125.5 (4)	H36—C36—C37	120.2
H14—C14—C15	117.2	C36—C37—H37	119.6
C14—C15—C16	119.7 (3)	C36—C37—C38	120.8 (4)
C14—C15—C20	124.2 (4)	H37—C37—C38	119.6
C16—C15—C20	115.9 (4)	C33—C38—C37	120.5 (3)
C15—C16—H16	119.2	C33—C38—H38	119.7
C15—C16—C17	121.7 (4)	C37—C38—H38	119.7
H16—C16—C17	119.2	Cu1—N5—C39	168.7 (3)
C16—C17—H17	120.0	N5—C39—S1	179.0 (4)
O1—N1—C1—C2	−173.1 (4)	O4—N4—C20—C15	−149.4 (4)
O1—N1—C1—C6	7.7 (6)	O4—N4—C20—C19	32.7 (5)
O2—N1—C1—C2	10.3 (6)	Cu1—P1—C21—C22	33.7 (3)

O2—N1—C1—C6	−168.9 (5)	Cu1—P1—C21—C26	−147.6 (3)
N1—C1—C2—C3	179.3 (4)	C27—P1—C21—C22	158.9 (3)
C6—C1—C2—C3	−1.5 (6)	C27—P1—C21—C26	−22.4 (3)
C1—C2—C3—C4	1.1 (6)	C33—P1—C21—C22	−93.8 (3)
C2—C3—C4—C5	0.0 (7)	C33—P1—C21—C26	84.9 (3)
C3—C4—C5—C6	−0.8 (7)	P1—C21—C22—C23	178.8 (3)
C4—C5—C6—C1	0.4 (6)	C26—C21—C22—C23	0.0 (5)
C4—C5—C6—C7	−177.1 (4)	C21—C22—C23—C24	0.2 (6)
N1—C1—C6—C5	179.9 (4)	C22—C23—C24—C25	−0.6 (6)
N1—C1—C6—C7	−2.8 (6)	C23—C24—C25—C26	0.8 (6)
C2—C1—C6—C5	0.7 (6)	P1—C21—C26—C25	−178.4 (3)
C2—C1—C6—C7	178.0 (4)	C22—C21—C26—C25	0.2 (5)
C1—C6—C7—C8	145.3 (4)	C24—C25—C26—C21	−0.6 (6)
C5—C6—C7—C8	−37.4 (6)	Cu1—P1—C27—C28	29.9 (3)
C6—C7—C8—C9	175.6 (4)	Cu1—P1—C27—C32	−147.6 (3)
Cu1—N2—C9—C8	−2.2 (6)	C21—P1—C27—C28	−94.0 (3)
C10—N2—C9—C8	179.4 (3)	C21—P1—C27—C32	88.5 (3)
C7—C8—C9—N2	−174.9 (4)	C33—P1—C27—C28	159.4 (3)
Cu1—N2—C10—C11	−48.3 (3)	C33—P1—C27—C32	−18.1 (3)
C9—N2—C10—C11	130.6 (4)	P1—C27—C28—C29	−177.5 (3)
Cu1—N3—C11—C10	−22.5 (4)	C32—C27—C28—C29	0.2 (5)
C12—N3—C11—C10	161.0 (3)	C27—C28—C29—C30	−0.7 (6)
N2—C10—C11—N3	47.6 (4)	C28—C29—C30—C31	0.0 (6)
Cu1—N3—C12—C13	1.0 (5)	C29—C30—C31—C32	1.2 (6)
C11—N3—C12—C13	176.9 (3)	C30—C31—C32—C27	−1.8 (6)
N3—C12—C13—C14	−178.9 (4)	P1—C27—C32—C31	178.5 (3)
C12—C13—C14—C15	−177.0 (4)	C28—C27—C32—C31	1.0 (5)
C13—C14—C15—C16	34.2 (6)	Cu1—P1—C33—C34	−151.3 (3)
C13—C14—C15—C20	−151.9 (4)	Cu1—P1—C33—C38	28.9 (3)
C14—C15—C16—C17	174.2 (4)	C21—P1—C33—C34	−27.4 (3)
C20—C15—C16—C17	−0.3 (6)	C21—P1—C33—C38	152.8 (3)
C15—C16—C17—C18	−0.5 (6)	C27—P1—C33—C34	81.4 (3)
C16—C17—C18—C19	0.9 (6)	C27—P1—C33—C38	−98.4 (3)
C17—C18—C19—C20	−0.5 (6)	P1—C33—C34—C35	−179.2 (3)
C18—C19—C20—N4	177.5 (4)	C38—C33—C34—C35	0.6 (5)
C18—C19—C20—C15	−0.4 (6)	C33—C34—C35—C36	0.7 (6)
C14—C15—C20—N4	8.7 (6)	C34—C35—C36—C37	−1.9 (6)
C14—C15—C20—C19	−173.4 (4)	C35—C36—C37—C38	1.9 (6)
C16—C15—C20—N4	−177.1 (3)	C36—C37—C38—C33	−0.7 (6)
C16—C15—C20—C19	0.7 (6)	P1—C33—C38—C37	179.2 (3)
O3—N4—C20—C15	31.9 (5)	C34—C33—C38—C37	−0.5 (5)
O3—N4—C20—C19	−146.1 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O2	0.95	2.31	2.640 (6)	100
C7—H7···O1	0.95	2.28	2.735 (5)	109

C7—H7···O3^{i}	0.95	2.54	3.468 (5)	165
C11—H11*B*···N5^{i}	0.99	2.59	3.339 (5)	133
C14—H14···O3	0.95	2.44	2.757 (5)	99
C14—H14···O1^{i}	0.95	2.48	3.387 (5)	159
C19—H19···O4	0.95	2.51	2.757 (6)	95
C24—H24···O2^{ii}	0.95	2.62	3.297 (6)	129
C28—H28···N5	0.95	2.61	3.471 (5)	151

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*+2, −*y*, −*z*+1.